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(71) Applicant (for all designated States except US): CANON KABUSHIKI KAISHA [JP/JP]; 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP).

(72) Inventor; and

(75) Inventor/Applicant (for US only): YONEHARA, Takao [JP/JP]; c/o Canon Kabushiki Kaisha, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP).

(74) Agent: OHTSUKA, Yasunori; 7th Fl., Shuwa Kioicho Park Bldg., 3-6, Kioicho, Chiyoda-ku, Tokyo 1020094 (JP).

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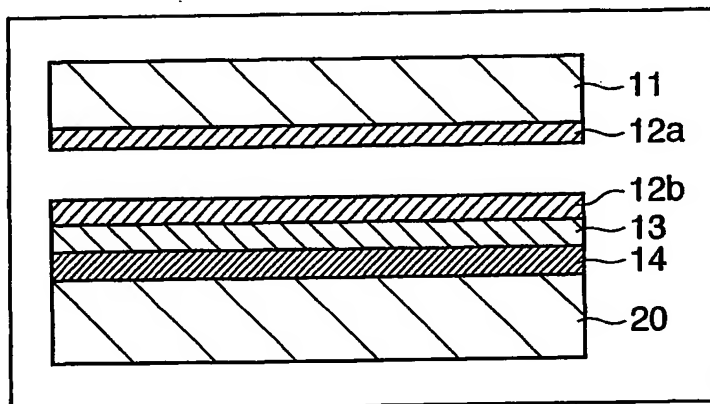
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(54) Title: SUBSTRATE, MANUFACTURING METHOD THEREFOR, AND SEMICONDUCTOR DEVICE



(57) Abstract: A step of forming the first substrate which has a separation layer and a Ge layer on the separation layer, and a step of forming a bonded substrate stack by bonding the first substrate to the second substrate through an insulating layer, and a step of dividing the bonded substrate stack at the separation layer are performed, thereby obtaining a substrate with a GOI structure.

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DESCRIPTION

SUBSTRATE, MANUFACTURING METHOD THEREFOR, AND
SEMICONDUCTOR DEVICE

5 TECHNICAL FIELD

The present invention relates to a substrate, a manufacturing method therefor, and a semiconductor device and, more particularly, to a substrate with a GOI (Germanium-On-Insulator) structure having a Ge
10 layer on an insulator, a manufacturing method therefor, and a semiconductor device.

BACKGROUND ART

In recent years, a substrate with an SOI
15 (Silicon-On-Insulator) structure having an Si layer on an insulator has received attention. For example, Japanese Patent Nos. 2,608,351, 2,877,800, and
3,048,201 each disclose a method of manufacturing such an SOI substrate.

20 There has recently been proposed a semiconductor device with a GOI (Germanium-On-Insulator) structure having a Ge layer on an insulator. A semiconductor device with a GOI structure is expected to be superior to a semiconductor device with an SOI structure
25 particularly in performance speed. For example, (USP) 6,501,135 discloses a semiconductor device with a GOI structure and a method of manufacturing a GOI

substrate. The manufacturing method disclosed in ~~USP~~
~~6,501,135~~ bonds an Si substrate to an insulating film
formed on a Ge substrate, thereby obtaining a GOI
substrate. The GOI substrate is used to obtain a
5 semiconductor device which employs a thin Ge film
having a thickness of 500 Å as an active layer.

To obtain a semiconductor device which employs a
thin Ge film as an active layer using a GOI substrate
formed by bonding together a Ge substrate and an Si
10 substrate, as disclosed in ~~USP~~~~6,501,135~~, most of the
Ge substrate having a thickness of about several
hundred μm needs to be removed by polishing or
etching, prior to the step of forming the semiconductor
device. It is difficult to control the thickness of
15 the thin Ge film to be uniform in removing the Ge
substrate by polishing or the like. Accordingly, the
semiconductor device to be obtained cannot sufficiently
exhibit its superiority as a device with a GOI
structure. The semiconductor device is hard to
20 manufacture at high yield, and a process of removing
almost the entire part of the Ge substrate increases
the manufacturing cost.

DISCLOSURE OF INVENTION

25 The present invention has been made on the basis
of the above-mentioned background, and has as its
object to provide a method of manufacturing a GOI

substrate which sufficiently exhibits the superiority as a semiconductor device with a GOI structure and can ensure good economy.

According to the present invention, there is
5 provided a method of manufacturing a substrate which has a Ge layer on an insulating layer,, characterized by comprising steps of forming a first substrate which has a separation layer and a Ge layer on the separation layer, forming a bonded substrate stack by bonding the
10 first substrate to a second substrate through an insulating layer, and dividing the bonded substrate stack at the separation layer.

Other features and advantages of the present invention will be apparent from the following
15 description taken in conjunction with the accompanying drawings, in which like reference characters designate the same or similar parts throughout the figures thereof.

20 BRIEF DESCRIPTION OF DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles
25 of the invention.

Fig. 1 is a view for explaining a substrate manufacturing method according to a preferred

embodiment of the present invention;

Fig. 2 is a view for explaining the substrate manufacturing method according to the preferred embodiment of the present invention;

5 Fig. 3 is a view for explaining the substrate manufacturing method according to the preferred embodiment of the present invention;

Fig. 4 is a view for explaining the substrate manufacturing method according to the preferred
10 embodiment of the present invention;

Fig. 5 is a view for explaining the substrate manufacturing method according to the preferred embodiment of the present invention;

Fig. 6 is a view for explaining the substrate
15 manufacturing method according to the preferred embodiment of the present invention;

Fig. 7 is a view for explaining the substrate manufacturing method according to the preferred embodiment of the present invention;

20 Fig. 8 is a view for explaining the substrate manufacturing method according to the preferred embodiment of the present invention; and

Fig. 9 is a view for explaining a semiconductor device according to the preferred embodiment of the
25 present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

A preferred embodiment of the present invention will be described below with reference to the accompanying drawings.

Figs. 1 to 8 are views for explaining a method of manufacturing a GOI substrate according to the preferred embodiment of the present invention. In the step shown in Fig. 1, a semiconductor substrate 11 is prepared. In the step shown in Fig. 2, a separation layer 12 is formed on the surface of the semiconductor substrate 11. As the semiconductor substrate 11, an Si substrate or Ge substrate is preferable. As the separation layer 12, a porous layer formed by anodizing the surface of the semiconductor substrate 11 is preferably used. Anodization can be performed by, e.g., arranging an anode and cathode in an electrolytic solution containing hydrofluoric acid (HF), arranging a semiconductor substrate between the electrodes, and supplying a current between them. The porous layer may be made up of a plurality of, i.e., two or more layers having different porosities.

In the step shown in Fig. 3, a Ge layer 13 is formed on the separation layer 12 by epitaxial growth. The epitaxial growth on the porous layer serving as the separation layer 12 allows the Ge layer 13 to have a uniform thickness and good crystallinity. If an Si substrate is employed as the semiconductor substrate 11, the porous Si layer 12 between the Si substrate 11

and the Ge layer 13 can relax mismatch between the lattice constant of Si and that of Ge to obtain the Ge layer 13 with good crystallinity. On the other hand, when a Ge substrate is employed as the semiconductor substrate 11, no lattice constant mismatch occurs, and the Ge layer 13 with better crystallinity can be obtained.

Instead of the processes shown in Figs. 2 and 3, for example, a method of implanting ions such as hydrogen ions at a predetermined depth from the surface of the semiconductor substrate 11 in the state shown in Fig. 1 to form an ion-implanted layer as the separation layer 12 may be adopted. In this case, a Ge substrate is preferably employed as the semiconductor substrate 11, and a portion on the surface side as viewed from the separation layer 12 serves as the Ge layer 13.

In the step shown in Fig. 4, an insulating layer 14 is formed on the Ge layer 13. In the above-mentioned manner, a first substrate 10 having the Ge layer 13 on the porous layer or ion-implanted layer serving as the separation layer 12 is formed. As the insulating layer 14, silicon dioxide (SiO_2) can be used. Other preferable examples of the insulating layer 14 include an oxide film of silicon oxynitride (SiON), aluminum oxide (Al_2O_3), hafnium oxide (HfO_2), zirconium oxide (ZrO_2), tantalum oxide (Ta_2O_5), and the like.

In the step shown in Fig. 5, a second substrate 20 is bonded to the surface of the first substrate 10 shown in Fig. 4 to form a bonded substrate stack 30.

Typically, an Si substrate or a substrate obtained by forming an insulating film such as an SiO_2 layer on its surface is preferably employed as the second substrate 20. Also, any other substrate such as a glass substrate may be employed as the second substrate 20.

In the step shown in Fig. 6, the bonded substrate stack 30 is divided into two substrates by cutting it at the separation layer 12. This division can be performed by, e.g., a method of using a fluid. As the method, a method of forming a jet of a fluid (liquid or gas) and injecting the jet to the separation layer 12, a method which utilizes the static pressure of a fluid, or the like is preferably employed. Out of jet injection methods, a method using water as the fluid is called a wafer jet method. The division can also be performed by annealing the bonded substrate stack 30. Such division by annealing is particularly effective when an ion-implanted layer is formed as the separation layer 12. Alternatively, the division may be performed by inserting a solid member such as a wedge into the separation layer 12.

In the step shown in Fig. 7, a separation layer 12b left on the Ge layer 13 of the second substrate 20 is removed using an etchant or the like. At this time,

the Ge layer 13 is preferably used as an etching stopper layer. Then, a planarization step such as a hydrogen annealing step, polishing step, or the like may be performed as needed to planarize the Ge layer

5 13.

With the above-mentioned operation, a semiconductor substrate 40 shown in Fig. 8 is obtained. The semiconductor substrate 40 shown in Fig. 8 has the thin Ge layer 13 on its surface and the insulating

10 layer 14 immediately below the Ge layer 13. The expression "thin Ge layer" is intended to mean a layer thinner than a general semiconductor substrate. To exhibit the superiority as a semiconductor device, the thickness of the Ge layer 13 preferably falls within a

15 range of 5 nm to 2 μ m. A gallium arsenide (GaAs) layer can be formed on the Ge layer 13, depending on the specifications of the semiconductor device. Since mismatch between the lattice constant of Ge and that of GaAs is small, a GaAs layer with good crystallinity can

20 be obtained.

After the bonded substrate stack 30 is divided in the step shown in Fig. 6, a separation layer 12a left in the first substrate 10 is removed using an etchant or the like. Then, the hydrogen annealing step,

25 polishing step, or the like may be performed to planarize the first substrate 10. The planarized substrate may be reused as the semiconductor substrate

11 to be used in the step shown in Fig. 1. Repeated use of the semiconductor substrate 11 can greatly reduce the manufacturing cost of a GOI substrate.

As has been described above, the manufacturing method according to the present invention makes it possible to obtain a GOI substrate which has a thin Ge film with a uniform thickness and good crystallinity. Also, the manufacturing method according to the present invention can greatly reduce the manufacturing cost of a GOI substrate.

[Examples]

Preferred examples of the present invention will be described below.

(Example 1)

15 A first p-type Si substrate 11 with a resistivity of $0.01 \Omega \cdot \text{cm}$ was prepared. Then, the first Si substrate 11 was anodized in an anodizing solution to form a porous Si layer serving as a separation layer 12. The anodizing conditions were as follows.

20 Current density: $7 \text{ (mA/cm}^2\text{)}$

Anodizing solution: $\text{HF} : \text{H}_2\text{O} : \text{C}_2\text{H}_5\text{OH} = 1 : 1 : 1$

Time: 11 (min)

Thickness of porous silicon: 12 (μm)

The current density and the concentrations of the respective components of the anodizing solution can appropriately be changed in accordance with the thickness, structure, and the like of the separation

layer (porous Si layer) 12 to be formed. Preferably, the current density falls within a range of 0.5 to 700 mA/cm², and the ratio between the concentrations of the components of the anodizing solution falls within a
5 range of 1 : 10 : 10 to 1 : 0 : 0.

The porous Si layer is useful because a high-quality epitaxial Ge layer is formed thereon, and the porous Si layer functions as the separation layer. The thickness of the porous Si layer is not limited to
10 that of the above example. Good results can be obtained as far as the thickness falls within a range of, e.g., 0.1 μ m to several hundred μ m.

The anodizing solution only needs to contain HF and need not contain ethanol. Ethanol, however, is
15 useful for removing any air bubbles from the surface of the substrate and is preferably added to the anodizing solution. Examples of a chemical agent which has a function of removing air bubbles include, e.g., alcohols such as methyl alcohol and isopropyl alcohol,
20 a surfactant, and the like in addition to ethanol. Instead of adding these chemical agents, air bubbles may be eliminated from the substrate surface by vibrations of ultrasonic waves or the like.

The anodized substrate was oxidized in an oxygen
25 atmosphere at 400°C for 1 hr. With this oxidation step, the inner walls of pores of the porous Si layer were covered with a thermally oxidized film. A Ge

layer 13 having a thickness of 0.3 μm is epitaxially grown on the porous Si layer by chemical vapor deposition (CVD). The growth conditions were as follows.

5 Source gas: GeH_4/H_2

Gas flow rate: 0.5/180 L/min

Gas pressure: 80 Torr

Temperature: 600°C

Growth rate: 0.3 $\mu\text{m}/\text{min}$

10 Note that these growth conditions can appropriately be changed in accordance with required specifications of the Ge layer 13.

Then, Zr was deposited to a thickness of 200 nm on the surface of the epitaxial Ge layer 13 by
15 sputtering in an ultrahigh vacuum at room temperature. The first Si substrate 11 was oxidized with ozone in situ in the same chamber to form a ZrO_2 layer 14.

The surface of a first substrate 10 and that of a second substrate 20 were put together and brought into
20 contact with each other. The first substrate 10 and second substrate 20 were subjected to annealing at 800°C for 5 min, thereby increasing the bonding strength. With this operation, a bonded substrate stack 30 was obtained.

25 Pure water was injected from a 0.1-mm nozzle of a water jet apparatus toward a concave portion (concave portion formed by the beveled portions of the two

substrates 10 and 20) of the periphery of the bonded substrate stack 30 in a direction parallel to the bonding interface of the bonded substrate stack 30 at a high pressure of 50 MPa. With this operation, the bonded substrate stack 40 was cut at the separation layer 12 and divided into two substrates. The pressure of the pure water preferably falls within a range of, e.g., several MPa to 100 MPa.

In this division step, any one of the following operations may be performed.

(1) The nozzle performs scanning such that a jet of pure water injected from the nozzle moves along the concave portion formed by the beveled portions.

(2) The bonded substrate stack 30 is held by a wafer holder and rotates on its axis to inject pure water into the concave portion formed by the beveled portions around the periphery of the bonded substrate stack.

(3) The operations (1) and (2) are performed in combination.

Consequently, the ZrO_2 layer 14, epitaxial Ge layer 13, and a part 12b of the porous Si layer 12, which were originally formed on the side of the first substrate 10 were transferred to the side of the second substrate 20. Only the porous Si layer 12a was left on the surface of the first substrate 10.

Instead of dividing (separating) the bonded

substrate stack by a water jet method, a jet of gas may be used or a solid wedge may be inserted into the separation layer of the bonded substrate stack.

Alternatively, a mechanical force such as a tensile
5 force, shearing force, or the like may be applied to the bonded substrate stack or ultrasonic waves may be applied to the bonded substrate stack. In addition, any other method may be adopted.

The porous Si layer 12b which was transferred to
10 the uppermost surface of the second substrate 20 was selectively etched using an etchant in which at least a 49% hydrofluoric acid (HF) solution, a 30% hydrogen peroxide (H_2O_2) solution, and water (H_2O) were mixed.

The Ge layer 13 was left unetched while the porous Si
15 layer 12b was selectively etched and completely removed. If the selective etching is performed while rotating the substrate and starting/stopping generating ultrasonic waves using an apparatus combined with a circulator which circulates the etchant, non-uniform
20 etching on the surface of each substrate and among substrates can be suppressed. Additionally, if an alcohol or surfactant is mixed with the etchant, unevenness in etching caused by reactive air bubbles on the surface can be suppressed.

25 The etching speed of the Ge layer with the etchant is extremely low, and the selectivity ratio to the etching speed of the porous layer reaches 10^5 or

more. The etching amount in the Ge layer can practically be neglected.

With the above-mentioned steps, a semiconductor substrate which has the Ge layer 13 with a thickness of 0.3 μm on the ZrO_2 layer 14 was obtained. Although the porous Si layer was selectively etched, no change occurred in the Ge layer 13. When the film thickness of the formed Ge layer 13 was measured at 100 points across the surface, the uniformity of the film thickness was $301 \text{ nm} \pm 4 \text{ nm}$.

The observation of the cross section with a transmission electron microscope showed that the Ge layer 13 maintained good crystallinity.

Furthermore, the substrate was subjected to annealing in a hydrogen atmosphere at 600°C for 1 hr, and the surface roughness of Ge was evaluated with an atomic force microscope. The mean square roughness in a $50\text{-}\mu\text{m}$ -square region was about 0.2 nm, which was equivalent to that of a commercially available Si wafer.

The surface may be planarized by polishing such as CMP, instead of hydrogen annealing.

If plasma processing is performed for at least one of respective surfaces to be bonded of the first and second substrates as a preprocess of the bonding step, the bonding strength can be increased even by annealing at a low temperature. Additionally, a

substrate having undergone plasma processing is preferably washed with water.

In the division step, a plurality of bonded substrate stacks may be arranged in their planar direction, and a nozzle of a water jet apparatus may perform scanning along the planar direction, thereby continually dividing the plurality of bonded substrate stacks.

Alternatively, a plurality of bonded substrate stacks may be arranged in a direction perpendicular to each plane, and a nozzle of a water jet apparatus may be provided with an X-Y scanning function. Then, a jet of water may sequentially be injected toward a plurality of bonding portions of the bonded substrate stack, and the bonded substrate stacks may automatically be divided.

After the division step, the porous Si layer 12a left on the first substrate 10 was removed, and the first substrate 10 was subjected to planarization. Reuse of the planarized substrate in the formation step of the first substrate can reduce the manufacturing cost of a GOI substrate. Repeated reuse can greatly reduce the manufacturing cost of the GOI substrate.

(Example 2)

This example is an improved example of Example 1 and is the same as Example 1 except for anodizing conditions.

In this example, an Si substrate 11 was prepared and anodized in a solution containing HF under either of the following anodizing conditions.

(First Anodizing Condition)

5 (First Step)

Current density: 8 (mA/cm²)

Anodizing solution: HF : H₂O : C₂H₅OH = 1 : 1 : 1

Time: 11 (min)

Thickness of porous silicon: 13 (μm)

10 (Second Step)

Current density: 22 (mA/cm²)

Anodizing solution: HF : H₂O : C₂H₅OH = 1 : 1 : 1

Time: 2 (min)

Thickness of porous silicon: 3 (μm)

15 or

(Second Anodizing Condition)

(First Step)

Current density: 8 (mA/cm²)

Anodizing solution: HF : H₂O : C₂H₅OH = 1 : 1 : 1

20 Time: 5 (min)

Thickness of porous silicon: 6 (μm)

(Second Step)

Current density: 33 (mA/cm²)

Anodizing solution: HF : H₂O : C₂H₅OH = 1 : 1 : 1

25 Time: 1.3 (min)

Thickness of porous silicon: 3 (μm)

The first porous Si layer to be formed at the

first step of the anodization is used to form a high-quality epitaxial Ge layer thereon. The second porous Si layer to be formed under the first porous Si layer at the second step of the anodization is used as
5 a separation layer.

(Example 3)

An FET with the structure shown in Fig. 9 was formed on a semiconductor substrate manufactured by each of the methods described in Examples 1 and 2. A
10 gate insulating film 41 made of zirconium oxide (ZrO_2), a gate electrode 42 made of porous silicon, a channel region 43, and a source and drain region 44 were formed in a semiconductor substrate 40 with a GOI structure which has a Ge layer 13 on an insulating layer 14 made
15 of zirconium oxide (ZrO_2). As the gate insulating film 41, an oxide film of, e.g., aluminum oxide (Al_2O_3), hafnium oxide (HfO_2), tantalum oxide (Ta_2O_5), or the like may preferably be used in addition to zirconium oxide (ZrO_2). In this example, the FET was formed on
20 the semiconductor substrate manufactured by each of the methods described in Examples 1 and 2. The present invention, however, is not limited to this, and other semiconductor devices such as a transistor, diode, LSI, and the like can be formed.

25 (Other Example)

Various film forming techniques such as CVD, MBE, sputtering, liquid phase growth can be applied to an

epitaxial growth step for forming a Ge layer.

Also, various other etchants (e.g., a mixture of a hydrofluoric acid solution, nitric acid solution, and acetic acid solution) can be applied to a step of
5 selectively etching a separation layer (porous layer, ion implantation layer, or the like) left upon division, in addition to a mixture of a 49% hydrofluoric acid solution, a 30% hydrogen peroxide solution, and water as described above.

10 As many apparently widely different embodiments of the present invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the
15 appended claims.

CLAIMS

1. A method of manufacturing a substrate which has a Ge layer on an insulating layer, comprising steps of:
forming a first substrate which has a separation
5 layer and a Ge layer on the separation layer;
forming a bonded substrate stack by bonding the first substrate to a second substrate through an insulating layer; and
dividing the bonded substrate stack at the
10 separation layer.
2. The method according to claim 1, wherein the insulating layer is formed on the Ge layer.
3. The method according to claim 1, wherein the insulating layer is formed on the second substrate.
- 15 4. The method according to claim 1, wherein the separation layer is formed by porosifying a semiconductor substrate by anodization.
5. The method according to claim 1, wherein the separation layer is formed by implanting ions in a
20 semiconductor substrate.
6. The method according to claim 4, wherein the semiconductor substrate contains one of silicon and germanium.
7. The method according to claim 1, wherein the Ge
25 layer is formed by epitaxial growth.
8. The method according to claim 1, wherein the insulating layer includes an oxide film.

9. The method according to claim 1, wherein the insulating layer contains silicon dioxide (SiO_2).

10. The method according to claim 1, wherein the insulating layer contains at least one of silicon oxynitride (SiON), aluminum oxide (Al_2O_3), hafnium oxide (HfO_2), zirconium oxide (ZrO_2), and tantalum oxide (Ta_2O_5).

11. The method according to claim 1, wherein the division step includes a step of dividing the separation layer by a jet of a fluid or a static pressure.

12. The method according to claim 1, wherein the division step includes a step of dividing the separation layer by annealing the bonded substrate stack.

13. The method according to claim 1, wherein the division step includes a step of dividing the separation layer by inserting a member into the separation layer.

14. The method according to claim 1, further comprising a step of removing a part of the separation layer left on the Ge layer on the second substrate after the division step.

15. The method according to claim 1, further comprising a step of planarizing a surface of the Ge layer after the division step.

16. The method according to claim 1, further

comprising a step of removing a part of the separation layer left on the first substrate after the division step.

17. The method according to claim 1, further
5 comprising a step of planarizing a surface of the first substrate and reusing the planarized first substrate in the step of forming the first substrate after the division step.

18. A substrate which is manufactured by a method of
10 manufacturing a substrate as defined in claim 1.

19. A semiconductor device which is manufactured using a substrate which is manufactured by a method of manufacturing a substrate as defined in claim 1.

FIG. 1

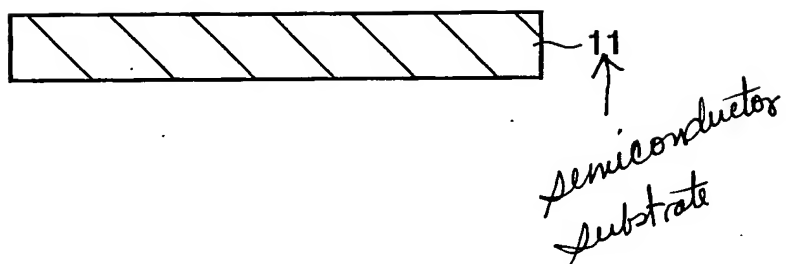


FIG. 2

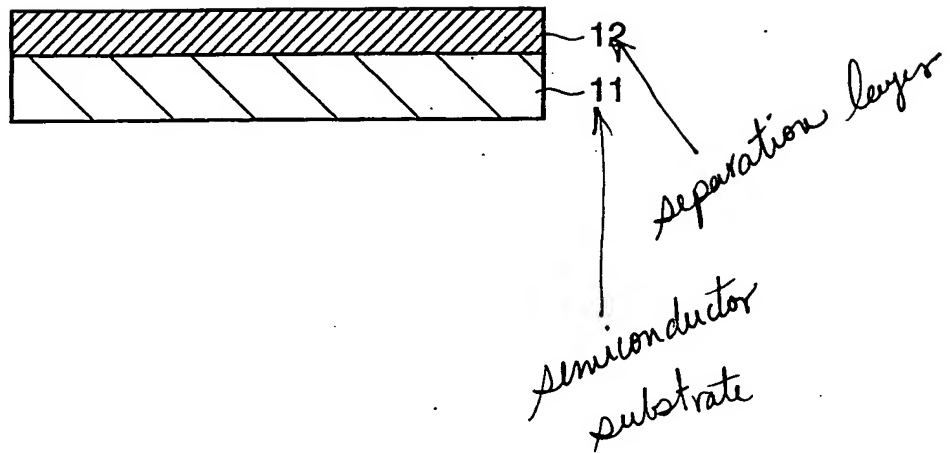


FIG. 3

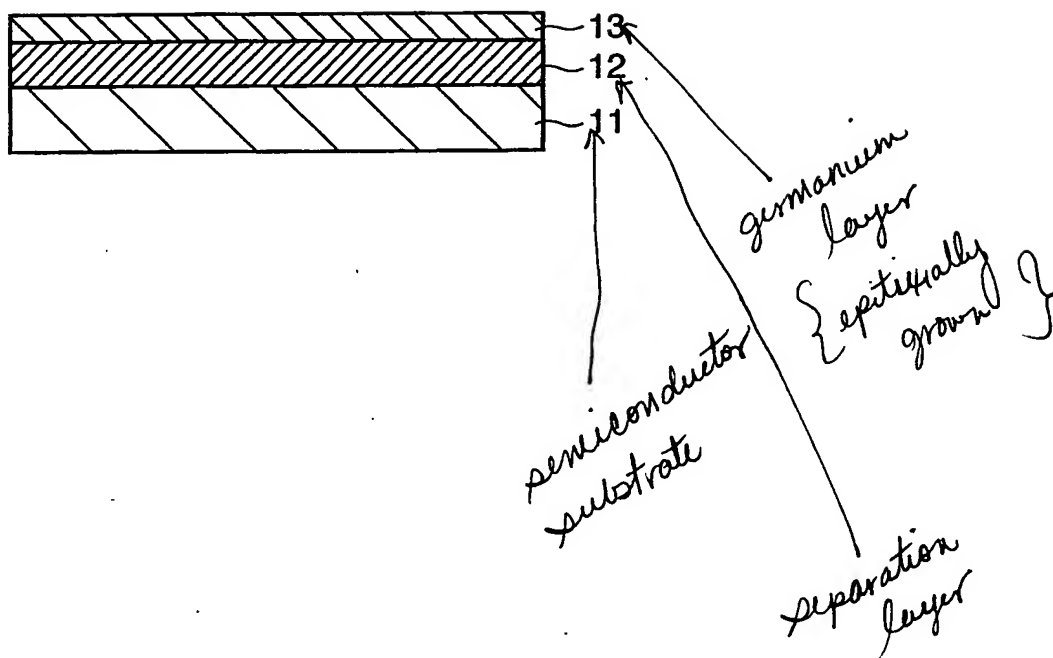


FIG. 4

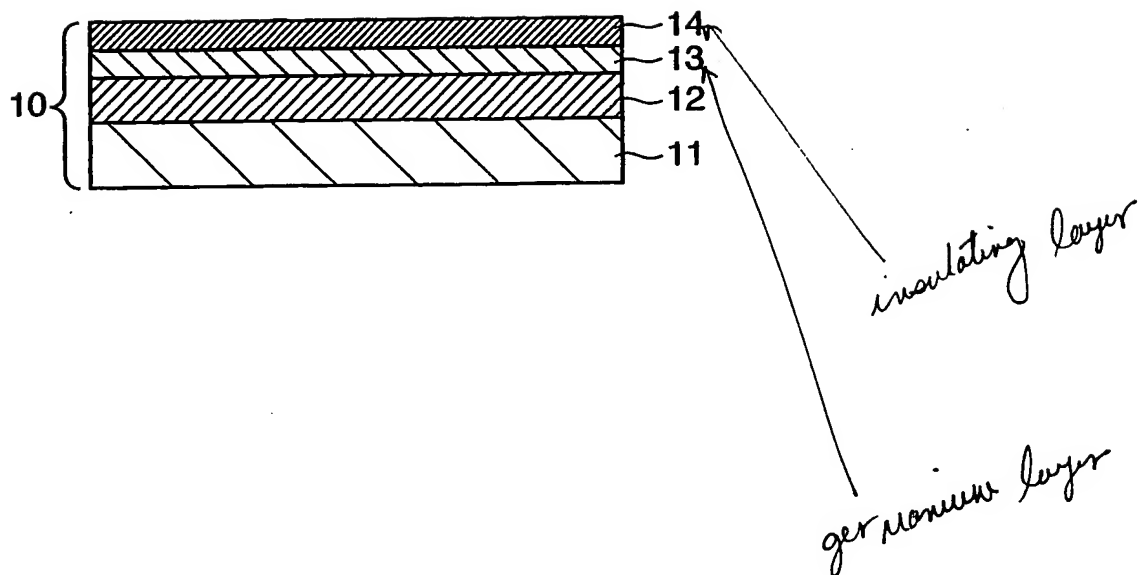


FIG. 5

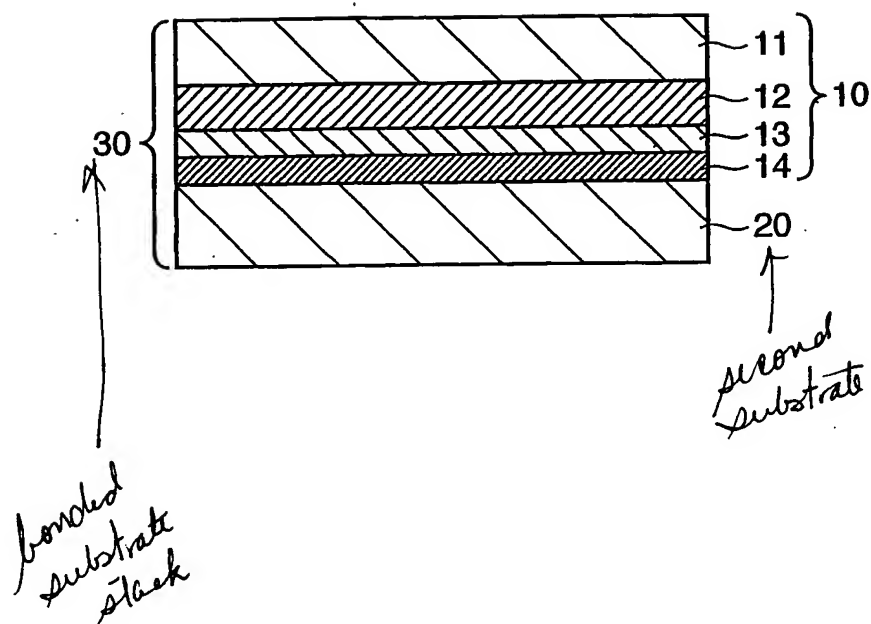
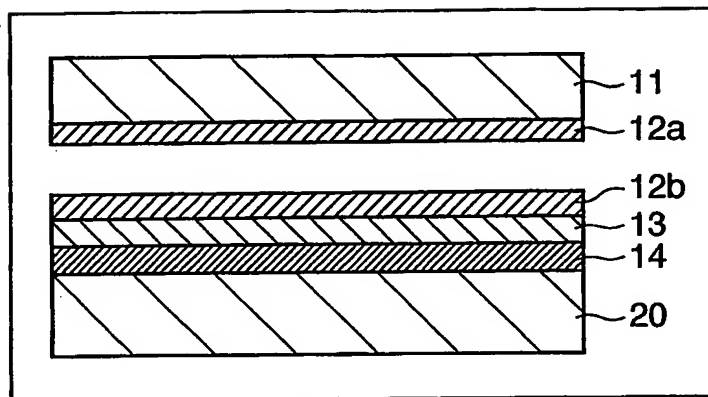


FIG. 6



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FIG. 7

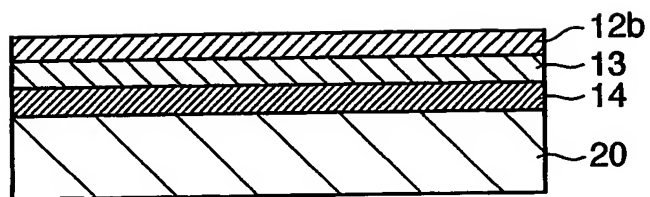


FIG. 8

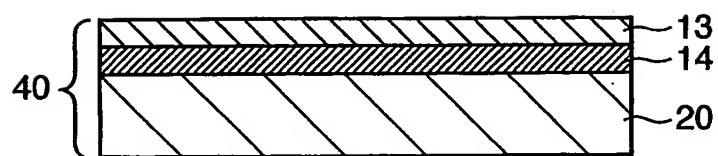
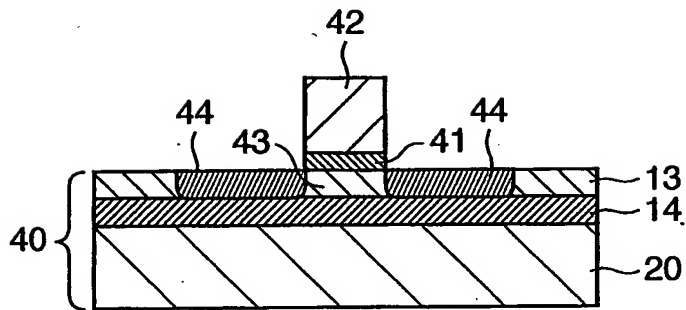


FIG. 9



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP 2004/006176

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl⁷ H01L27/12, H01L21/76

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl⁷ H01L21/02, H01L21/76, H01L27/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
 Japanese Utility Model Gazette 1922-1996, Japanese Publication of Unexamined Utility Model Applications 1971-2004, Japanese Registered Utility Model Gazette 1994-2004, Japanese Gazette Containing the Utility Model 1996-2004

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 867919 A2 (CANON KABUSHIKI KAISHA) 1998.09.30, see whole document, Figs.1A-7	1-9, 13-19
Y	see whole document, Figs.1A-7 & JP 10-326884 A, whole document, Figs.1-7 & US 2003/190794 A1	8-12
X	EP 1050901 A2 (CANON KABUSHIKI KAISHA) 2000.11.08, see whole document, Figs.1A-13G	1, 2, 4-9, 11-19
Y	see whole document, Figs.1A-13G & JP 2001-15721 A, whole document, Figs.1-14 & US 6605518 B1	3, 10
Y	JP 6-196674 A (CANON KABUSHIKI KAISHA) 1994.07.15, see [0041], Figs.1-9 (Family:none)	10



Further documents are listed in the continuation of Box C.



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Name and mailing address of the ISA/JP

Japan Patent Office

3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan

Authorized officer

TAKASHI WATAHIKI

Telephone No. +81-3-3581-1101 Ext. 3460

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 4-361555 A (HITACHI LTD) 1992.12.15, see [0059], Figs.1-6 (Family:none)	10
Y	JP 2001-168308 A (CANON KABUSHIKI KAISHA) 2001.06.22, see [0102], Figs.1-8 & US 6653209 B1	10